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Abstract

5 A process is provided for preparing light-colored isocyanates which can be used for preparing urethane compounds, in particular polyurethanes, for example polyurethane foams.

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

ATTORNEY DOCKET NUMBER IN-12101	U.S. APPLICATION NO. (IF KNOWN SEE 37 RR 15) 10/018636	
INTERNATIONAL APPLICATION NO. PCT/EP 00/05610	INTERNATIONAL FILING DATE 16.06.00	PRIORITY DATE CLAIMED 23.06.99

LIGHT-COLORED ISOCYANATES, THEIR PREPARATION AND THEIR USE

Martin REIF; Peter Van Den ABEEL; Filip NEVEJANS; Hans VOLKMAR; Ulrich PENZEL; and Volker SCHARR.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:


1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
 2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
 3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371 (b) and PCT Articles 22 and 39(1).
 4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date
 5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
 6. ☒ A translation of the International Application into English (35 U.S.C. 371(C)(2)).
 7. ☒ Amendment to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☒ are transmitted herewith (required only if not transmitted by the International Bureau).
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 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made
 8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
 9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
 10. ☐ A translation of the annex to the International Preliminary Examination Report under PCT Article 36
- Items 11. to 16. below concern other document(s) or information included:**
11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
 12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included
 13. ☒ A FIRST preliminary amendment.
 14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
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 16. ☒ A Change of power of attorney and/or address letter.
 17. ☒ Other items or information: Postcard

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LORI D. HASS


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17. <input checked="" type="checkbox"/> The following fees are submitted				CALCULATIONS PTO USE ONLY	
Basic National Fee (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO..... \$890.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) \$710.00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))..... \$740.00 Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO..... \$1,040.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)..... \$100.00					
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Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	
Claims	Number Filed	Number Extra	Rate		
Total Claims	22 - 20 =	2	X \$18.00	36.00	
Independent claims	1 - 03 =	0	X \$84.00	\$0.00	
Multiple dependent claims(s) (if applicable)			+ \$280.00	\$0.00	
TOTAL OF ABOVE CALCULATION				=	\$926.00
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				\$	
SUBTOTAL				=	\$926.00
Processing fee of \$130.00 for furnishing the English translation later the <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				+	\$
TOTAL NATIONAL FEE				=	\$926.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				+	\$40.00
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NOTE: Where an appropriate time limit under 37 CFR 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

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34,780
REGISTRATION NUMBER

PATENT

(Docket No. IN-12101)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

MARTIN REIF ET AL

Serial No.: NEW

Group Art Unit: NEW

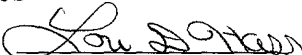
Filed: HEREWITH

Examiner: NEW

For: LIGHT-COLORED
ISOCYANATES, THEIR
PREPARATION AND THEIR USE

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Lori D. Hass

PRELIMINARY AMENDMENT**BOX PCT APPLICATION**

Assistant Commissioner of Patents
Washington, D.C. 20231

Sir:

In reference to the above-referenced patent application, please enter the following
amendment and consider the accompanying remarks prior to examination thereof on the merits.

IN THE CLAIMS:

Please cancel claims 8 and 9.

Please amend the claims as follows:

3. A process as claimed in claim 1, wherein the reaction is carried out in a solvent.
4. A process as claimed in claim 1, wherein the amine used is an amine of the diphenylmethanediamine series or a mixture thereof.
5. A process as claimed in claim 1, wherein the process is carried out in one or two stages.
6. A process as claimed in claim 1, wherein the reaction is carried out under super-atmospheric pressure or atmospheric pressure.
7. An isocyanate prepared according to a process as claimed in claim 1.

Please add the following new claim:

10. A process as claimed in claim 2, wherein the reaction is carried out in a solvent.
11. A process as claimed in claim 2, wherein the amine used is an amine of the diphenylmethanediamine series or a mixture thereof.
12. A process as claimed in claim 3, wherein the amine used is an amine of the diphenylmethanediamine series or a mixture thereof.
13. A process as claimed in claim 2, wherein the process is carried out in one or two stages.
14. A process as claimed in claim 3, wherein the process is carried out in one or two stages.
15. A process as claimed in claim 4, wherein the process is carried out in one or two stages.
16. A process as claimed in claim 2, wherein the reaction is carried out under super-atmospheric pressure or atmospheric pressure.

17. A process as claimed in claim 3, wherein the reaction is carried out under super-atmospheric pressure or atmospheric pressure.
18. A process as claimed in claim 4, wherein the reaction is carried out under super-atmospheric pressure or atmospheric pressure.
19. A process as claimed in claim 5, wherein the reaction is carried out under super-atmospheric pressure or atmospheric pressure.
20. An isocyanate prepared according to a process as claimed in claim 2.
21. An isocyanate prepared according to a process as claimed in claim 3.
22. An isocyanate prepared according to a process as claimed in claim 4.
23. An isocyanate prepared according to a process as claimed in claim 5.
24. An isocyanate prepared according to a process as claimed in claim 6.

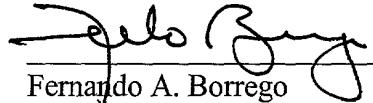
REMARKS

Applicants respectfully request examination of the present application as amended herein. Claims 8 and 9 have been cancelled. Claims 3-7 have been amended. Claims 10-24 have been added. Upon entry of the above preliminary amendment, claims 1-7 and 10-24

remain pending in the application. A marked up version of the amended claims is attached hereto in Appendix A. Should the Examiner have any questions, please contact the undersigned attorney.

Respectfully submitted,

Date: 12/12/01


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APPENDIX A - Amended Claims

3. (Amended) A process as claimed in claim 1 [or 2], wherein the reaction is carried out in a solvent.

4.(Amended) A process as claimed in [any of claims 1 to 3] claim 1, wherein the amine used is an amine of the diphenylmethanediamine series or a mixture [of two or more such amines] thereof.

5. (Amended) A process as claimed in [any of claims 1 to 4] claim 1, wherein the process is carried out in one or two stages.

6. (Amended) A process as claimed in [any of claims 1 to 5] claim 1, wherein the reaction is carried out under super-atmospheric pressure or atmospheric pressure.

7. (Amended) An isocyanate [able to be] prepared [by] according to a process as claimed in [any of claims 1 to 6] claim 1.

Please add the following new claim:

10. (New) A process as claimed in claim 2, wherein the reaction is carried out in a solvent.

11. (New) A process as claimed in claim 2, wherein the amine used is an amine of the diphenylmethanediamine series or a mixture thereof.

12. (New) A process as claimed in claim 3, wherein the amine used is an amine of the diphenylmethanediamine series or a mixture thereof.

13. (New) A process as claimed in claim 2, wherein the process is carried out in one or two stages.

14. (New) A process as claimed in claim 3, wherein the process is carried out in one or two stages.

15. (New) A process as claimed in claim 4, wherein the process is carried out in one or two stages.

16. (New) A process as claimed in claim 2, wherein the reaction is carried out under super-atmospheric pressure or atmospheric pressure.

17. (New) A process as claimed in claim 3, wherein the reaction is carried out under super-atmospheric pressure or atmospheric pressure.

18. (New) A process as claimed in claim 4, wherein the reaction is carried out under super-atmospheric pressure or atmospheric pressure.

19. (New) A process as claimed in claim 5, wherein the reaction is carried out under super-atmospheric pressure or atmospheric pressure.

20. (New) An isocyanate prepared according to a process as claimed in claim 2.

21. (New) An isocyanate prepared according to a process as claimed in claim 3.

22. (New) An isocyanate prepared according to a process as claimed in claim 4.

23. (New) An isocyanate prepared according to a process as claimed in claim 5.

24. (New) An isocyanate prepared according to a process as claimed in claim 6.

BASF Aktiengesellschaft

as originally filed

Light-colored isocyanates, their preparation
and their use

5 The present invention relates to light-colored isocyanates, a process for preparing light-colored isocyanates and also their use in urethane compounds, in particular in polyurethanes, for example in polyurethane foams.

10 Isocyanates and isocyanate mixtures are prepared by known methods by phosgenation of the corresponding amines. For polyurethane foams, use is made, for example, of bifunctional or polyfunctional aromatic isocyanates of the diphenylmethane diisocyanate series (MDI). Due to the preparation process, the phosgenation and subsequent work-up (removal of the solvent; separation of monomeric MDI) often results in dark-colored products which in turn give yellowish polyurethane foams or other, likewise discolored PUR materials. This is undesirable, since such discoloration adversely affects the overall visual impression and allows slight inhomogeneities to occur, e.g. as streaks in the foams obtained. Light-colored isocyanates or isocyanates which contain a reduced amount of color-imparting components are therefore preferred as raw materials.

25 There have always been many attempts to obtain polyisocyanates, in particular ones of the diphenylmethane diisocyanate series, having a light color. Numerous methods are known for empirically lightening the color of MDI. However, the nature of the troublesome colored substances has hitherto been elucidated only to an
30 unsatisfactory degree.

The previously known methods can be divided into four groups:

1. Processes in which the starting material diamino-diphenylmethane (MDA) or its oligomers have been subjected to treatment and/or purification

EP-A 0 546 398 describes a process for preparing polymeric MDI in which the polymethylene-polyphenylene-polyamine used as starting material is acidified prior to phosgenation.

EP-A 0 446 781 relates to a process for preparing polymeric MDA (monomeric and oligomeric polymethylene-polyphenylene-polyamines) which are firstly treated with hydrogen and subsequently subjected to a phosgenation, with a relatively light-colored MDI being obtained.

The abovementioned methods give only a slight improvement in the color, since the colored substances in the MDI have been found on the basis of experience to be formed not only from certain MDA secondary components but also to result from color precursors which are formed by secondary reactions during the phosgenation.

25

2. Process engineering solutions in the phosgenation process

US-A 5 364 958 relates to a process for preparing polyisocyanates in which, after the phosgenation, the phosgene is removed completely at low temperature and the isocyanate is subsequently treated hot with HCl gas.

DE 19817691.0 describes a process for preparing MDI/-PMDI mixtures having a reduced content of chlorinated

by-products and a reduced iodine color number by adherence to defined parameters in the phosgenation reaction. In particular, adherence to particular phosgene/HCl ratios in the reaction step are required here. This process has the disadvantage that a variation of the parameters in the phosgenation is made difficult and the quality of the phosgenation is very sensitive as a result. In addition, the lack of flexibility in the parameters in the phosgenation makes the phosgenation very difficult to carry out in practice and requires a high engineering outlay.

Although processes of the type mentioned attempt to remove discoloring components at the correct point, they are not efficient enough, both because of their high engineering outlay or the high costs and also in terms of their color-lightening effect, since only slight degradation of color precursors occurs due to incomplete chemical reactions.

3. Addition of color-lightening additives to the crude isocyanate product obtained after the phosgenation and before the work-up

EP-A 0 581 100 relates to a process for preparing polyisocyanates in which a chemical reducing agent is added after the phosgenation and before the removal of solvent, which according to this document likewise gives light-colored products.

According to US-A 4 465 639, water is added to the crude product obtained after the phosgenation in order to lighten its color. EP-A 538 500, EP-A 0 445 602 and EP-A 0 467 125 describe the addition of carboxylic acids, alkanols or polyether polyols after the phosgenation for the same purpose.

Although the above-described methods of lightening the color are efficient, they have disadvantages in that the additives not only lighten the color but also undergo reactions with the isocyanates obtained as product, generally resulting, for example, in an undesirable reduction in the isocyanate content. In addition, there is the risk of formation of undesirable by-products in the MDI.

4. After-treatment of the end product

EP-A 0 133 538 describes the purification of isocyanates by extraction, giving fractions of a light-colored MDI.

EP-A 0 561 225 describes a process for preparing isocyanates or isocyanate mixtures which, according to this document, contain no color-imparting components, in which process the isocyanates obtained after the phosgenation of the corresponding amines are subjected to a hydrogen treatment at a pressure of from 1 to 150 bar and a temperature of from 100 to 180°C. According to the examples described there, isocyanate end products are hydrogenated as such or in the form of their solutions in suitable solvents.

These color-improving after-treatments of the isocyanate end products after complete removal of the solvent at elevated temperature are likewise not very efficient, since the high temperatures occurring during the work-up, in particular during the distillation of the solvent and (in the case of the preparation of polymeric MDI) the removal of monomeric MDI, have already resulted in the formation of stable colored

substances which can be chemically degraded only with difficulty.

It is an object of the present invention to provide a new process for preparing isocyanates which contain no or only small amounts of color-imparting components. A further object of the invention is to provide a process for preparing isocyanates which, without the above-mentioned treatment steps, leads to light-colored isocyanates which are suitable for producing polyurethanes or their precursors which have no color or only a slight color.

We have found that this object is achieved by preparing the isocyanates using phosgene which contains less than 50 ppm of bromine or bromine-containing compounds or iodine or iodine-containing compounds.

The present invention accordingly provides a process for preparing isocyanates by reacting an amine or a mixture of two or more amines with phosgene containing less than 50 ppm of bromine or iodine or their mixtures in molecular or bound form.

For the purposes of the present text, bromine or iodine in molecular form means molecules which consist entirely of bromine or iodine atoms. Bromine or iodine in bound form means molecules which comprise not only bromine or iodine but also atoms different from the specified atoms.

The phosgene used for the purposes of the present invention thus contains less than 50 ppm of bromine or bromine compounds or iodine or iodine compounds; or bromine and iodine; or bromine and iodine and bromine compounds; or iodine compounds and bromine and iodine;

or bromine compounds and iodine compounds; or bromine and iodine and bromine compounds and iodine compounds.

5 The process of the present invention leads to isocyanates which, if desired even without the above-described additional treatments, can be used for preparing urethane compounds such as polyurethanes or their precursors which have no color or only a slight color.

10 The result obtained according to the present invention was particularly surprising because it had hitherto not been recognized that even extremely small traces of molecular or bound bromine or iodine or the above-mentioned mixtures in the phosgene used for the
15 preparation of isocyanates are sufficient to influence the product color in an undesirable way.

The phosgene used for the preparation of isocyanates generally has a certain content of molecular or bound
20 bromine or iodine or the abovementioned mixtures. The content of bromine or iodine or such mixtures in the phosgene results from the chlorine used for preparing the phosgene, since the chlorine usually contains a certain proportion of bromine or iodine or both. The
25 content of bromine or iodine or both in the chlorine generally results from the corresponding content in the salt used for producing the chlorine. However, it was previously not recognized that the bromine or BrCl present in the chlorine leads to formation of dibromo-
30 phosgene or bromochlorophosgene in the phosgene synthesis (analogous to the formation of COBrF from CO + BrF₃; see W. Kwasnik in "Handbuch der präparativen anorganischen Chemie", editor: G. Brauer, Volume 1, 3rd Edition, Ferdinand Enke Verlag, Stuttgart, 1975, p.
35 224). These compounds are said to react similarly to phosgene with amines to form isocyanates and hydrogen

bromide (US 2 733 254). Analogous reactions may be assumed for iodine.

5 The phosgene having a low content of bromine or iodine
or the abovementioned mixtures and used for the
purposes of the present invention can be prepared in
various ways known to those skilled in the art. One
possible way of guaranteeing a low content of bromine
or iodine or the abovementioned mixtures in the
10 phosgene is, for example, the use of starting compounds
which have a correspondingly low content of bromine or
iodine or both in the preparation of the phosgene. In
particular, the use of chlorine having an appropriately
low content of bromine or iodine or both is a
15 possibility here.

Methods of preparing suitable chlorine having a low
content of bromine or iodine or both are known to those
skilled in the art. In principle, the present invention
20 can be carried out using any chlorine which meets the
abovementioned specification, i.e. contains less than
about 50 ppm of bromine or iodine or the abovementioned
mixtures, for example 25 ppm or less. Thus, for
example, it is possible to use chlorine which has been
25 prepared by the electrolysis process or by the
oxidation of HCl, for example by the Deacon process. US
3,660,261 describes the preparation of chlorine having
a particularly low bromine content by oxidative treat-
ment of the salt used for the electrolysis. An alterna-
30 tive possibility is the removal of bromine or iodine or
both from chlorine by means of distillation, selective
condensation of the bromine or iodine in the stream of
chlorine or by reactions with substances which react
selectively with bromine or iodine or both, as
35 described, for example, in JP 0075319. Naturally, it is
also possible to use appropriate starting materials

which contain essentially no bromine or iodine in the chlorine synthesis, e.g. essentially bromine- and iodine-free salt or bromine- and iodine-free HCl. Suitable processes are described, for example, in DE-A 18 00 844, DE-B 12 55 643 or DE-A1 197 26 530.

A further possible way of preparing low-bromine chlorine is described in Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, Volume A6, p. 463 and Figure 70 on p. 465: when gaseous bromine-rich chlorine is subjected to a countercurrent scrub with liquid low-bromine chlorine, the chlorine gas to be purified is depleted in bromine and the liquid chlorine is enriched with bromine. To start up such a plant, the provision of a sufficient amount of low-bromine liquid chlorine is necessary; subsequently, a substream of the relatively low-bromine chlorine obtained can be liquefied and used for scrubbing the relatively bromine-rich chlorine. This process is carried out in columns containing customary internals which aid separation, for example trays, random packing or ordered packing. The achieved degree of depletion of bromine or iodine or both depends on the system pressure, the flow rates, the concentrations and the internals in the usual way for absorption and distillation processes; the design of the column given the desired degree of bromine depletion is therefore a purely routine task.

The largely bromine- and iodine-free chlorine obtained in this way can subsequently be converted into phosgene in customary and known processes as are described, for example, in Ullmanns Enzyklopädie der industriellen Chemie, 3rd Edition, Volume 13, pages 494-500.

A further way of obtaining phosgene having a low content of molecular or bound bromine or iodine or both

is to remove molecular and bound bromine and iodine from the phosgene itself. Here too, it is once again possible in principle to use all customary separation methods, for example distillation, adsorption and the like. As far as the process of the present invention is concerned, the only important thing is to adhere to the abovementioned upper limit for the concentration of molecular or bound bromine or iodine or the abovementioned mixtures.

10

In a preferred embodiment of the invention, use is made of phosgene having a content of bromine or iodine or the above-mentioned mixtures of less than 40 ppm, 35 ppm, 30 ppm or 25 ppm or less, in particular of 10 ppm or less.

15

The preparation of isocyanate taking place in the process of the present invention is carried out in a manner known to those skilled in the art by reacting an amine or a mixture of two or more amines with a superstoichiometric amount of phosgene. It is in principle possible to employ all methods in which a primary amine or a mixture of two or more primary amines is reacted with phosgene to form one or more isocyanate groups.

20

In a preferred embodiment of the invention, the process of the present invention, i.e. the reaction of the amine or the mixture of two or more amines with the phosgene, is carried out in a solvent or a mixture of two or more solvents.

25

As solvent, it is possible to use all solvents suitable for the preparation of isocyanates. These are preferably inert aromatic, aliphatic or alicyclic hydrocarbons or their halogenated derivatives. Examples of such solvents are aromatic compounds such as mono-

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- chlorobenzene or dichlorobenzene, for example o-dichlorobenzene, toluene, xylenes, naphthalene derivatives such as tetralin or decalin, alkanes having from about 5 to about 12 carbon atoms, e.g. hexane, heptane, octane, nonane or decane, cycloalkanes such as cyclohexane, inert esters and inert ethers such as ethyl acetate or butyl acetate, tetrahydrofuran, dioxane or diphenyl ether.
- As amines, it is in principle possible to use all primary amines which can react appropriately with phosgene to give isocyanates. Suitable amines are, in principle, all linear or branched, saturated or unsaturated aliphatic or cycloaliphatic or aromatic primary monoamines or polyamines, provided that these can be converted into isocyanates by means of phosgene. Examples of suitable amines are 1,3-propylenediamine, 1,4-butylenediamine, 1,5-pentamethylenediamine, 1,6-hexamethylenediamine and the corresponding higher homologues of this series, isophoronediamine (IPDA), cyclohexyldiamine, cyclohexylamine, aniline, phenylenediamine, p-toluidine, 1,5-naphthylenediamine, 2,4- or 2,6-toluenediamine or a mixture thereof, 4,4'-, 2,4'- or 2,2'-diphenylmethanediamine or mixtures thereof and also higher molecular weight isomeric, oligomeric or polymeric derivatives of the abovementioned amines and polyamines. In a preferred embodiment of the present invention, the amine used is an amine of the diphenylmethanediamine series or a mixture of two or more such amines.

After going through the process of the present invention, the abovementioned compounds are in the form of the corresponding isocyanates, e.g. as hexamethylene 1,6-diisocyanate, isophorone diisocyanate, cyclohexyl isocyanate, cyclohexyl diisocyanate, phenyl isocyanate,

- phenylene diisocyanate, 4-tolyl isocyanate, naphthylene 1,5-diisocyanate, tolylene 2,4- or 2,6-diisocyanate or mixtures thereof, diphenylmethane 4,4'-, 2,4'- or 2,2'-diisocyanate or mixtures of two or more thereof, or
5 else higher molecular weight oligomeric or polymeric derivatives of the abovementioned isocyanates or as mixtures of two or more of the abovementioned isocyanates or isocyanate mixtures.
- 10 In a preferred embodiment of the present invention, the amines used are the isomeric, primary diphenylmethane-diamines (MDA) or their oligomeric or polymeric derivatives, i.e. the amines of the diphenylmethanediamine series. Diphenylmethanediamine, its oligomers or poly-
15 mers are obtained, for example, by condensation of aniline with formaldehyde. Such oligoamines or polyamines or mixtures thereof are also used in a preferred embodiment of the invention.
- 20 The reaction of the low-bromine and low-iodine or even bromine-free and iodine-free phosgene which falls within the abovementioned restrictions and is to be used for the purposes of the present invention with one of the abovementioned amines or a mixture of two or
25 more such amines can be carried out continuously or batchwise in one or more stages. If a single-stage reaction is carried out, this reaction preferably takes place at from about 60 to 200°C, for example at from about 130 to 180°C.
- 30 In a further embodiment of the invention, the reaction can, for example, be carried out in two stages. Here, in a first stage, the reaction of the phosgene with the amine or the mixture of two or more amines is carried
35 out at from about 0 to about 130°C, for example from about 20 to about 110°C or from about 40 to about 70°C,

with a time of from about 1 minute to about 2 hours being allowed for the reaction between amine and phosgene. Subsequently, in a second stage, the temperature is increased to from about 60 to about 190°C, in particular from about 70 to 170°C, over a period of, for example, from about 1 minute to about 5 hours, preferably over a period of from about 1 minute to about 3 hours.

10 In a preferred embodiment of the invention, the reaction is carried out in two stages.

During the reaction, superatmospheric pressure can, in a further preferred embodiment of the invention, be applied, for example up to about 100 bar or less, preferably from about 1 bar to about 50 bar or from about 2 bar to about 25 bar or from about 3 bar to about 12 bar. However, the reaction can also be carried out under atmospheric pressure.

20 In a further preferred embodiment of the invention, the reaction is accordingly carried out at ambient pressure, generally about 1 bar. In a further preferred embodiment, the reaction can also be carried out at a pressure below ambient pressure.

Excess phosgene is preferably removed at from about 50 to 180°C after the reaction. The removal of remaining traces of solvent is preferably carried out under reduced pressure, for example the pressure should be about 500 mbar or less, preferably less than 100 mbar. In general, the various components are separated off in the order of their boiling points; it is also possible to separate off mixtures of various components in a single process step.

The present invention further provides light-colored isocyanates as can be prepared by the process of the present invention.

5 The invention further provides for the use of isocyanates which can be prepared by the process of the present invention or by such a process for preparing urethane compounds, in particular polyurethanes. In a preferred embodiment of the invention, the isocyanates
10 of the invention are used for producing polyurethane foams as are commercially available as, for example, rigid foams, semirigid foams, integral foams and flexible foams.

15 The invention is illustrated by the following examples.

In all examples, the bromine content in the phosgene was calculated from the bromine content of the chlorine used for the phosgene synthesis. The bromine content of
20 the chlorine was determined by means of X-ray fluorescence analysis.

The viscosities reported in the examples were determined on a Lauda CD 20 viscometer at 25°C.

25

Example 1: Preparation of the MDI samples:

100 g of polymeric MDA dissolved in 1.3 liters of monochlorobenzene are reacted under atmospheric pressure at
30 50-80°C with 200 g of phosgene dissolved in 1.3 liters of monochlorobenzene in a 6 liter stirred reactor. The temperature is increased to about 120°C over a period of 1-2 hours, during which time the reaction to form the isocyanates (125 g) takes place. Residual phosgene
35 and monochlorobenzene are subsequently distilled off under gentle conditions (110°C, 100 mbar). The solvent-

free crude MDI sample is subsequently after-treated for 45 minutes at 180°C and a pressure of 10 mbar.

5 The phosgenations of Examples 1 to 3 were carried out under the same conditions. The experiments differed only in the bromine content of the phosgene.

Example 1:

- 10 a. Phosgene having a bromine content of less than 10 ppm was used for the synthesis.
- b. Phosgene having a bromine content of 50 ppm was used for the synthesis.
- 15 c. Phosgene having a bromine content of 100 ppm was used for the synthesis.

20 The property data for the products are shown in Table 1.

Property data for the end products:

25 The property data for the isocyanate products prepared as Examples 1 to 3 were determined. In particular, the iodine color number customarily reported for MDI was determined. For this purpose, the samples (diluted 1:5 with monochlorobenzene) were measured on a photometer (from Dr. Lange, Berlin) in the program mode for the

30 iodine color number.

Table 1: Property data for the examples

	Bromine content of the phosgene (ppm)	NCO ¹ (%)	ICN ²
Example 1	< 10	32.2	18.9
Example 2	50	32.2	24.1
Example 3	100	32.3	28.6

¹ = NCO content (determined in accordance with ASTM
D 5155)

² = iodine color number

The results demonstrate a good lightening of the color
of crude MDI when using low-bromine chlorine.

Example 2:

In an industrial process, 7.9 metric tons/h of crude
MDA were reacted with 20.6 metric tons/h of phosgene in
chlorobenzene as process solvent at 95°C in a cascade
of stirred vessels to form the isocyanate. The mixture
leaving the phosgenation was freed of phosgene and
chlorobenzene and after-treated thermally according to
the prior art. Subsequently, some monomeric MDI was
separated from the crude MDI obtained in this way, so
that a polymeric MDI having a viscosity of about
200 mPas was obtained. The isocyanate property data
were determined on this product (Table 2).

Table 2: Isocyanate property data for Example 2

	Bromine content of the phosgene (ppm)	NCO (%)	ICN
Example 2a	40	31.5	15
Example 2b	20	31.5	12
Example 2c	10	31.5	10

Example 3:

In an industrial process, 3.3 metric tons/h of crude MDA were reacted with 9.2 metric tons/h of phosgene in chlorobenzene as process solvent in a valve tray column at a bottom temperature of 110°C to form the isocyanate. Excess phosgene and process solvent were subsequently distilled off at from 130 to 180°C in a sequence of a plurality of distillation columns. The isocyanate property data were determined on this product (Table 3).

Table 3: Isocyanate property data for Example 3

	Bromine content of the phosgene (ppm)	NCO (%)	ICN
Example 3a	120	31.7	26
Example 3b	70	31.7	18
Example 3c	30	31.6	13

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*as originally filed***We claim:**

1. A process for preparing isocyanates by reacting an amine or a mixture of two or more amines with phosgene containing less than 50 ppm of bromine or iodine or their mixtures in molecular or bound form.
2. A process as claimed in claim 1, wherein the phosgene contains less than 25 ppm of bromine or iodine or mixtures thereof in molecular or bound form.
3. A process as claimed in claim 1 or 2, wherein the reaction is carried out in a solvent.
4. A process as claimed in any of claims 1 to 3, wherein the amine used is an amine of the diphenylmethanediamine series or a mixture of two or more such amines.
5. A process as claimed in any of claims 1 to 4 carried out in one or two stages.
6. A process as claimed in any of claims 1 to 5, wherein the reaction is carried out under super-atmospheric pressure or atmospheric pressure.
7. An isocyanate able to be prepared by a process as claimed in any of claims 1 to 6.
8. The use of isocyanates able to be prepared as claimed in any of claims 1 to 6 or of an isocyanate as claimed in claim 7 for preparing urethane compounds.

9. The use as claimed in claim 8, wherein the urethane compounds are polyurethanes.

SECRET

DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

INVENTORSHIP IDENTIFICATION

My residence, post office address and citizenship are as stated below next to my name, I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

SPECIFICATION IDENTIFICATION

the specification of which

☐ is attached hereto.

☐ was filed on _____ as

Application Serial No. _____

and was amended on _____ (if applicable).

☒ was filed as PCT international application

Number PCT/EP00/05610

on 16/06/2000

and was amended under PCT Article 19

on _____ (if applicable)

ACKNOWLEDGMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information known by me to be material to the patentability of this application in accordance with Title 37, Code of the Federal Regulations. §1.56(a).

☐ In compliance with this duty there is attached an information disclosure statement. 37 CFR 1.97.

☒ In compliance with this duty, information which may be material is disclosed in the specification of the subject application.

CLAIM FOR BENEFIT OF EARLIER U. S. / PCT APPLICATION(S) UNDER 35 U. S. C. 120

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) or PCT international application(s) designating the United States of America that is / are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that / those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national of PCT international filing date of this application.

U. S. Application(s) (or PCT applications designating U. S.)

U. S. Application Serial No.	Filing Date	Status (pending, patented, abandoned)
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

RELATED FOREIGN APPLICATIONS

Related foreign applications, if any, filed in the name of the inventor(s) or the inventor(s) assigns more than twelve months before the filing of the subject application are as follows

Country	Application No.	Date of filing	Date of issue or publication
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

POWER OF ATTORNEY

I hereby appoint the following attorney(s) and agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected herewith:

12-
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Reg. No. 34,780;
Reg. No. 33,592;
Reg. No. 34,584;
Reg. No. 41,026;
Reg. No. 35,881;
Reg. No. 36,814;
Reg. No. 31,278;
Reg. No. 42,024;
Reg. No. 33,772;
Reg. No. 30,977;
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each of the above attorney(s) and agent(s) to have full powers of substitution and revocation, and each and any attorney or agent so substituted to have full powers of substitution and revocation.

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CLAIM FOR BENEFIT OF FOREIGN PRIORITY UNDER 35 U. S. C. §119

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United State of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

- ☐ No such applications have been filed.
☒ Such applications have been filed as follows

**DETAILS OF FOREIGN APPLICATION FROM WHICH PRIORITY CLAIMED
UNDER 35 U. S. C. §119**

Country	Application No.	Date of filing	Date of issue or publication
Germany	19928741.4	23 June 1999	

59 Ulrich Penzel
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